Appendix X

DETERMINATION OF PERCHLORATE IN WATER USING ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

Determination of Perchlorate in Water using Ion Chromatography with Suppressed Conductivity Detection

OBJECTIVE

To analyze perchlorate in reagent water, surface water, ground water, and finished drinking water using ion chromatography with suppressed conductivity detection.

The Groundwater Analysis Laboratory (GAL) has established a reagent water Method Detection Limit (MDL). Based on this MDL study, the GAL will report data at the Minimum Reporting Limit for perchlorate in all water samples at 4 ppb, a value slightly higher than the calculated Minimum Reporting Limit (MRL). This was done to avoid repeated QC failures at the ICCS (Initial Calibration Check Standard).

The GAL will report any perchlorate detected between the Laboratory's established MDL and the Minimum Reporting Limit as "trace present" and will not be report it as a quantitated concentration.

The MDL for a different matrix may differ from the one listed above depending upon the nature of the matrix and the procedure used.

REQUIRED AND RECOMMENDED MATERIALS

Equipment and Supplies

Ion Chromatograph (IC) – Analytical system consisting of plastic eluent reservoir bottles, a suitable liquid pump, injection valve, guard column, analytical separation column, electrical suppressor, conductivity detector, and computer based data acquisition system.

Anion Guard Column – Dionex AG16, 4 mm i.d. (P/N 55377) or equivalent.

Anion Separation Column – Dionex AS16, 4 mm i.d. (P/N 55376) or equivalent.

Anion Suppressor Device – Dionex Anion Self Regenerating Suppressor (4 mm ASRS, ULTRA, P/N 53946), or equivalent.

Detector – Conductivity Cell with temperature control (Dionex CD20 (P/N 44095), conductivity cell with temperature control (P/N 44130) or equivalent)

Chromatography Oven – Thermostat temperature control of chromatography temperature (Dionex LC25).

Data Acquisition System – Dionex PeakNet6 Data Chromatography Software or equivalent.

Conductivity Meter - At a minimum, this meter should be capable of measuring matrix conductance over a range of 1 – 10,000 μS/cm.

Bottles – High density polyethylene (HDPE) or glass, amber or clear, 30 ml, 125ml, and 250 ml.

Particulate Filters – 0.45 micron syringe filters for IC applications (Gelman IC Acrodisc- P/N 4485, or equivalent).

Disposable 5 mL syringes, used during sample preparation.

Analytical balance, accurate to +/- 0.0001g.

Weigh boats, spatulas in various sizes, micro-pipettes in various sizes TD (to deliver), micro-pipette tips in varying sizes, and class A volumetric flasks in varying sizes.

Self adhesive labels for labeling prepared standards and/or dilutions.

Indelible black ink pens.

NOTE* This laboratory will use the Dionex AG16 guard column with the Dionex AS16 separator column based on the recommendation of the EPA Method 314.0, section 6.1.2.1. Column comparison studies are also found in the same method in Table 4, on page 39.

Reagents and Standards

Reagent Water – Distilled, deionized water having a resistance of 18.0 MΩ or better, free from anions of interest. Water should contain particles no larger than 0.45 microns.

Eluent solution – 100 mM sodium hydroxide (made by dissolving 8.0 grams of 50% (W/W) sodium hydroxide in reagent water to a final volume of 1.0 L, Fisher, SS254-500).

Perchlorate stock solution, 100 µg/ml – A stock standard solution purchased as a certified solution from Accustandard (IS-6352-0.5X).

Sources of anions which are used to prepare a solution for the maximum conductivity threshold :

Sodium Chloride from Fisher Scientific, BP358-1

Sodium Sulfate, Fisher, BP354-500

Sodium Carbonate, Fisher, BP357-1

Use each of the above at 25 mg/ml anion concentrations. This solution is used to prepare simulated common anion samples in the determination of the matrix conductivity threshold (MCT).

Conductivity meter calibration solution – Potassium Chloride (KCl), Fisher, BP366-500

Sodium Perchlorate, Aldrich Chemicals, 7601-89-0 (100 g). This solid powder is used to prepare a quality control standard (QCS) as a second source of perchlorate to verify the calibration.

SUMMARY OF METHOD

A 1.0 ml volume of sample is introduced into an ion chromatograph (IC). Perchlorate is separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

NOTE*

This large sample loop (1.0 ml) can be made using approximately 219 cm (86 inches) of 0.03 inch i.d. PEEK tubing. The exact volume of the sample loop is not critical since all standards and samples will use the same loop. However, the volume should be verified to be within 5% of this volume by weighing the sample loop empty, filling the loop with deionized water, and reweighing the loop. Assuming the density of water to be 1.0 mg/µL can approximate the volume.

PROCEDURES

Initial Calibration Curve

Establish ion chromatographic operating parameters equivalent to those indicated in Table I .

Estimate the Linear Calibration Range (LCR). The LCR should cover the expected concentration range of field samples and should not extend over two orders of magnitude in concentration. The GAL will use five calibration standards in the range of 4.0 µg/L to 200 µg/L.

Prepare blank and working calibration standards by carefully adding accurately measured volumes of the stock standard to a volumetric flask and diluting to volume with reagent water. Record all dilutions and standard preparations in appropriate logs. The lowest calibration standard must be at the laboratory reporting limit. Prepare the calibration concentrations as follows:

Label five, 250-ml volumetric flasks with the different concentrations of the calibration standard i.e. 4.0 ppb, 50 ppb, 100 ppb, 150 ppb, 200 ppb.

Take aliquots of the Perchlorate stock solution at 100 ppm (µg/ml) and add these to the labeled volumetric flasks. Fill each flask to volume with mili-Q water according to Table II.

Pour 15 mL of a calibration standard/sample into a micro beaker. Using a 5 mL Luer lock syringe, draw up approximately 5 mL of standard, attach a 0.45 micron filter to the syringe and filter the standard, directly into the auto-sampler vial. Repeat with new filters and syringes for each sample or standard.

•Place auto-sampler vials in the correct order of ascension (starting with a blank, 4.0 ppb, followed by 50 ppb and ending with 200 ppb) in the auto-sampler tray.

•Place auto-sampler tray in the auto-sampler.

•Prepare a sequence table for the calibration standards specifying the Perchlorate method on the PeakNet6 Software.

Initial Calibration Check Standard (ICCS):

Analyze your lowest calibration standard again and use it as the Initial Calibration Check Standard (ICCS) to verify your initial calibration. Percent recovery of perchlorate must be in the range of 90-110%. If the 10 % recovery criteria is not met, re-evaluate the method/system and recalibrate followed by another ICCS.

Verify the accuracy and the acceptability of the instrument performance by analyzing a Quality Control Sample (QCS), an externally prepared second source at a concentration level that is near the middle of the calibration curve. The standard should fall within the ± 10 % recovery rule above. If the check does not meet acceptance criteria, re-evaluate the method/system and recalibrate followed by verification.

Establish a method detection limit (MDL) by analyzing seven replicates of laboratory fortified reagent water and process through the entire analytical method over a three day period.

Add 100 µL of 100 ppm stock perchlorate standard to a 25 mL volumetric flask and fill to volume to make a solution at the concentration of 400 µg/L (ppb). Take 2.5 mL of the 400 ppb intermediary standard and add it to a 25 mL volumetric flask and fill to volume to get a concentration of 2.5 ppb.

Take seven aliquots of the above dilution to make seven replicates.

Analyze the seven replicates and also record the retention time of each run to check for a reliable retention time for perchlorate.

Calculate the MDL based on the results of the above data by using the formula below:

Calculate the standard deviation (s) of the seven replicate measurements using formula:

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}$$

Where:

Xi; i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots (i.e. seven).

X is the mean for the n sample aliquots.

Calculate the MDL using the following formula:

$$MDL = t_{(n-1,\ 1-\alpha = 0.99)}(s)$$

Where:
$t_{(n-1,\ 1-\alpha = 0.99)}$ = the analyst's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Verify the MDL by taking an analyte concentration that is 2-3 times the MDL and analyzing it.

NOTE* The MDLs should be verified periodically depending on changing conditions of the instrument. Every new analyst must determine a new MDL and may not use the existing MDL determined by the previous analyst. The suggested concentrations in 4.4.1 may also change according to the changing conditions of the instrument.

Minimum Reporting Limit (MRL):
The Minimum reporting Limit should be set at 3-5 times the calculated MDL. The MRL can be set at the lowest level of the calibration curve or slightly above that. The MRL should never be set below the lowest calibration standard if an accurately quantified result is wanted. Any perchlorate recovered between the MDL and the MRL must be reported as "trace present" and flagged with the letter J as an estimated concentration.

Initial Demonstration of Accuracy (IDA):
Validate the accuracy of the method by analyzing seven replicates of laboratory fortified blanks (LFBs) fortified at 25 ppb of Perchlorate.

Take 25 µL of the 100 ppm stock perchlorate standard and add it a 100 mL volumetric flask. Fill to volume with reagent water to make a 25 ppb concentration.

Calculate their mean measured concentrations of the replicate values as follows:

$$(\bar{C}_x) = (C1 + C2 + C3 + \ldots.Cn) / n$$

where,

$(\bar{C}_x)$ = Mean recovered concentration of the replicate analysis.
C1, C2, …Cn = Recovered concentrations of the replicate 1, 2, ….n.
n = 7

To pass the IDA, the value derived for must be within 10 % of the true value or between 22.5 µg/L and 27.5 µg/L.

Initial Demonstration of Precision (IDP):
Using the data above, calculate the percent relative standard deviation (%RSD) of the replicate analysis using the formula below:

$$\% \text{ RSD} = \frac{S_{n-1}}{C_{\bar{x}}} \text{ x } 100\%$$

Where,

Sn-1 = sample standard deviation (n-1) of the replicate analyses.

$C_{\bar{x}}$ = mean recovered concentration of the replicate analysis.

The % RSD of the replicate analyses must be less than 10%.

Matrix Conductivity Threshold (MCT)
Determine the MCT by preparing a series of sequentially increasing, common anion fortified, reagent water samples, each containing a constant concentration of Perchlorate. Calibrate the Conductivity Meter before determining the MCT by following the procedure:

Conductivity Meter Calibration:

•Dissolve 0.745 g of Potassium Chloride (KCl) in reagent water and dilute to a final volume of 1.00 L in a volumetric flask (The reference conductance of this solution is 1410 µS/cm).

•Rinse the electrode in reagent water, place it in reagent water, turn on the meter and confirm that the conductance of this blank is < 1 µS/cm.

•Pour 15 mL of KCL solution into a beaker, place the electrode in the solution and measure the conductivity. (It should read between 1380 µS/cm and 1440 µS/cm to be in calibration).

•If the conductivity meter fails the calibration, recalibrate the unit per manufacture's instruction and then repeat the procedure.

Prepare a laboratory fortified reagent blank containing Perchlorate at a concentration of 25 ppb by adding 12.5 µL of the 100 ppm stock solution to a 50 mL volumetric flask and filling to volume with reagent water.

Prepare sequentially increasing ionic solutions each containing Perchlorate at the concentration of 25 ppb as follows:

Dissolve the following salts in reagent water to a final volume of 25.0 mL:

•1.0 g sodium chloride = 0.61 g Cl-

•0.93 g sodium sulfate =0.63 g SO4=

•1.1 g sodium carbonate = 0.62 g CO3=

Prepare the series of common anion fortified reagent water in 50 mL volumetric flasks as in Table III.

Measure and record conductance of each of the prepared solutions on a calibrated conductivity meter (section 4.8.1). Use the 400 mg/L mixed anion sample as a relative reference conductance. The conductance should be between 3200 µS/cm and 3700 µS/cm.

Analyze each solution on the PeakNet Software, recording the peak area to height (A/H) ratio and the quantified concentration of Perchlorate (See Table VII).

Calculate the A/H ratio percent difference (PDA/H) between the average A/H ratio for the LFB (A/HLFB) and the average A/H ratios for each mixed common anion solutions (A/HMA) using the following equation:

$$PD_{A/H} = \frac{|(A/H_{LFB} - A/H_{MA})|}{A/H_{LFB}} \times 100$$

NOTE*As the conductivity of the matrices increases, the PDA/H will increase. MCT is the matrix conductance where the PDA/H exceeds 20%.

Perform a linear regression on these data by plotting PDA/H (as the independent variable, x) verses the matrix conductance (as the dependent variable, y). The regression data must yield an r2 value of > 0.95. Record the constant (intercept value) and the " X – coefficient " (slope) and calculate the MCT as follows:

MCT = (20%) x (X-coefficient) + constant

Confirm the Perchlorate minimum reporting limit (MRL) by analyzing a mixed common anion solution that reflects a conductance near the above-specified MCT. The concentration of the Perchlorate must be at the laboratory determined MRL, while the concentration of the mixed common anion solution must be estimated near the MCT.

NOTE* The resulting conductance must be within ± 10% of the MCT and the measured Perchlorate must be between 80 – 120 % of the MRL concentration.

SAMPLE PREPARATION

During the preparation of all standards, special attention must be given to the expiration date of the stock perchlorate standards whether they are made in the laboratory or bought as certified standards from a manufacturer. Although the perchlorate stock standard may be stable for longer periods of time, stored at room temperature, do not store longer than 12 months. All the standards, stock and/or intermediary or working, must be labeled with an expiration date. Intermediary and working standards must be re-made after one month.

Bring all samples and standards to room temperature prior to analysis (in the temperature range of 24 °C ± 5 °C).

All sample batches must be accompanied by the QCS, IPCS, LRB, ICCS, LFB, LFM, LFMD, CCCS, and ECCS (See below for definitions).

Prepare the above standards as follows:

• QCS - Weigh 0.1231 g of the Sodium Perchlorate powder and add to a 1000 mL volumetric flask and fill to volume with reagent water. This will give you a stock standard at a concentration of 100 ppm (mg/L). Pipette 250 µL of this stock solution into a 250 mL volumetric flask and fill with reagent water to volume to get a concentration of 100 ppb

• IPCS – (See below for added assistance) – Follow:

[1] Prepare a laboratory fortified reagent blank containing Perchlorate at a concentration of 25 ppb by adding 12.5 µL of the 100 ppm stock solution to a 50 mL volumetric flask and filling to volume with reagent water.

[2] Dissolve the following salts in reagent water to a final volume of 25.0 mL:

• 1.0 g sodium chloride = 0.61 g Cl-

• 0.93 g sodium sulfate =0.63 g SO4=

• 1.1 g sodium carbonate = 0.62 g CO3=

[3] Remove 400 µL of the perchlorate in [1] and substitute it with 400 µL of the anion mixture in [2], This will give you a 25 ppb solution of perchlorate at the MCT (See Table III). Discard perchlorate waste in the assigned waste container.

• LRB – The reagent water from the MiliQ System.

• ICCS – Utilize the 4 ppb standard that was made for the generation of the calibration curve.

• LFB – Add 25 µL of 100 ppm stock perchlorate standard into a 100 mL volumetric flask and fill to volume with reagent water to make a concentration of 25 ppb.

• LFM – Add 2.5 mL of 100 ppm stock perchlorate solution to a 250 mL volumetric flask. Fill to volume to give an intermediary standard concentration of 1 ppm. Add 250 µL of the 1 ppm intermediary standard to 5 mL of sample. This will render a matrix spike concentration of 50 ppb.

• LFMD – Repeat the same procedure as in the LFM, using another aliquot of the same sample matrix.

• CCCS – Utilize the mid point standard from the calibration curve.

• ECCS – Utilize the end point standard from the calibration curve.

Determine the conductivity of the field samples by using a calibrated conductivity meter. If the conductance of the sample is above the laboratory MCT, dilute the sample before analysis or follow sponsor specifications regarding dilutions/pretreatments of project samples.

Estimate the dilution factor by dividing the matrix conductance by the MCT. Round up this value to the next whole number and dilute the sample by a proportion equivalent to this value.

Measure the conductance of the diluted sample to confirm it to be below the MCT. Analyze the sample with the understanding that MRL has been elevated by a proportion equal to the dilution factor.

Load and analyze the standards and samples in the sample sequence provided in Table IV, Appendix II. Use this table to analyze one data batch. Additional batches may be added sequentially provided all QC requirements are met for each batch.

The IPC must be analyzed at the beginning of every analytical batch in conformance to section 9.3.2.1 of EPA Method 314.0. Additionally, the IPC must be:

1. measured for conductance and the measured conductance should not exceed more than 10 % of the originally measured value. This value must be recorded in an appropriate log book. If the measured conductance is found to be more than 10 %, a new IPC solution must be prepared.
2. the percent difference between the area/height of the IPC and the area/height of the LFB in the original IDC or the IPC in the previous analytical batch must be calculated using equation in section 4.8.8. The percent difference must not be greater than 25 %. If the percent difference is greater than 25 %, corrective action(s) must be taken according to section 9.3.2.5 of EPA Method 314.0.
3. the recovery of perchlorate must fall between 80 % and 120 %. If recovery is outside this criterion then corrective action must be taken according to section 9.3.2.5 of EPA Method 314.0.
4. the retention time of the IPC must be recorded appropriately and care must be taken that the retention time does not shift more than 5 %. The column must be cleaned or replaced if the retention time shifts to less than 80 % of the originally recorded time (See section 9.3.2.4 of EPA Method 314.0).

QUALITY CONTROL CHECKS/ACCEPTANCE CRITERIA

Sample holding time must not exceeded 28 days.

At least a five point calibration curve must be generated with the MRL set no lower than the lowest calibration standard. The instrument must be re-calibrated as soon as or as often as any of the acceptance criteria given below are not met.

An IPC must accompany every analysis batch. Conductance of IPC solution must be within ± 10% of original conductance value for MCT. The calculated percent difference between the IPC and the LFB in the original IDC /or the IPC in the previous analytical batch must be no greater than 25 %.The quantitated Perchlorate value must be between 80-120% of the fortified level (20 ppb to 30 ppb for a 25ppb fortification). The retention time of the IPC must not shift by more than 5 %.

Initial Calibration Check Standard (ICCS) must verify each calibration. Recovery must be 10% of the true value in order to continue with the analysis.

A Laboratory Fortified Blank (LFB) at 25 ppb must follow the ICCS. Recovery must be 85-115 %. Sample batches that fail the LFB recovery limits must not be reported as valid.

A Continuing Calibration Check Standard (CCCS) and an End Calibration Check Standard (ECCS) at the mid and high level (alternating the two/10 samples) must continually monitor calibration. Recovery must be between 90-110%.

A Laboratory Reagent Blank (LRB), which must be analyzed prior to any sample, must be included in every analysis batch (up to 20 samples). The level of recovered perchlorate must be below the MDL in order to be accepted as a reagent blank. If it is >MDL, the analysis batch will not be considered valid.

A field or Laboratory Fortified Matrix (LFM), fortified matrix must accompany every sample batch. The LFM must be prepared at concentrations equal to or greater than the native sample concentration. The LFM should not be prepared at a concentration greater than 10 times the highest concentration observed in any field sample. If the recovery for Perchlorate is not between 80-120 %, and the recoveries for all other QC performance criteria are met, then the result for that LFM must be labeled as suspect matrix. Analyze also a duplicate of the LFM and calculate the Relative Percent Difference (RPD). RPD must be 15%. If the control criteria are not met for matrix spike results, all samples in the analytical batch must be re-analyzed. If the LFM fails the recovery criteria even after re-analysis, label sample as suspect matrix. If the control criteria are not met for the second matrix spike analysis, the results associated with the best matrix spike analysis shall be qualified "N" and reported.

WASTE DISPOSAL

The Perchlorate waste must be discarded in the containers provided by the Texas Tech Safety Services. The waste will be disposed according to the Texas Tech University Environmental Health and Safety guidelines.

LITERATURE CITED

Test Methods for Evaluating Solid Wastes, SW-846, Third Edition, through update II, September 1994.

"Determination of Perchlorate In Drinking Water by Ion Chromatography." U.S. EPA Method 314.0., Revision 1.0 November 1999, National Exposure Research Laboratory Office of Research and Development, Cincinnati, Ohio.

"Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection." U.S. EPA Method 9058, Revision 0, November 2000.

TABLES

Table I, Ion Chromatograph Operating Procedures.
Table II, Preparation of Calibration Standards.
Table III, Preparation of Common Anion Mixture with Perchlorate.
Table IV, Sample Analysis Table.
Table V, Determination of Method Detection Limits.
Table VI, Calculation of MDL
Table VII, Determination of Maximum Conductivity Threshold.

DEFINITIONS
MDL – Method Detection Limit
MCT – Matrix Conductivity Threshold
QCS – Quality Control Sample
IPCS – Instrument Performance Check Standard
LRB – Laboratory Reagent Blank
ICCS – Initial Calibration Check Standard
LFB – Laboratory Fortified blank
LFM – Laboratory Fortified Matrix
LFMD – Laboratory Fortified Matrix Duplicate
CCCS – Continuing Calibration Check Standard
ECCS – End Calibration Check Standard

Table I: Ion Chromatograph Operating Parameters

Ion Chromatograph:	Dionex IC25
Guard Column:	IonPac AG16 (4 x 50mm)
Analytical column:	IonPac AS16 (4 x 250)
Eluent:	100 mM NaOH
Eluent Flow:	1.0 mL /minute
Injection Volume:	1000 µL
Typical System Backpressure:	1200 – 2000 psi
Detection:	Suppressed conductivity, external water mode
Background Conductivity:	< 2-5 µS
Determined MCT:	3318 µS
Total method analysis time:	11 – 14 minute

Table II: Preparation of Calibration Standards

Volume of stock Perchlorate standard at 100ppm (microliters) used	Volumetric Flask (mL)	Final concentration (µg/L or ppb)
10	250	4
125	250	50
250	250	100
375	250	150
500	250	200

Table III: Preparation of common anion mixture with Perchlorate

Volume of common anion mixture (mL)	Perchlorate stock, at 100ppm added (µL)	Final concentration in 50 mL volume
0 µL	12.5	25.0 µg/L (ppb)
0.20	12.5	25.0 µg/L (ppb)

0.30	12.5	25.0 µg/L (ppb)
0.40	12.5	25.0 µg/L (ppb)
0.50	12.5	25.0 µg/L (ppb)
0.60	12.5	25.0 µg/L (ppb)
0.80	12.5	25.0 µg/L (ppb)
1.00	12.5	25.0 µg/L (ppb)

Table IV: Sample Analysis Sequence Table

Injection #	Sample Description	Acceptance Criteria
1	(IPCS) Instrument Performance Check Standard at MCT (25 ppb at 3318 µS/cm)	Recovery of 80-120%
2	QCS at calibration midpoint (100ppb)	Recovery of 90-110%
3	(LRB)Laboratory Reagent Blank	< MDL check sample
4	ICCS at the MRL (4.0 ppb)	Recovery of 90-110%
5	(LFB)Laboratory Fortified Blank (25ppb)	Recovery of 85-115%
6	Sample 1	Normal analysis
7	Sample 2	Normal analysis
8	Sample 3	Normal analysis
9	Sample 4	Normal analysis
10	Sample 5	Normal analysis
11	Sample 6	Normal analysis
12	Sample 7	Normal analysis
13	Sample 8	Normal analysis
14	Sample 9	Normal analysis
15	Sample 10	Normal analysis
16	CCCS (100ppb)	Recovery of 90-110
17	Sample 11	Normal analysis
18	Sample 12	Normal analysis
19	Sample 13	Normal analysis
20	Sample 14	Normal analysis
21	Sample 15	Normal analysis
22	Sample 15	Normal analysis
23	Sample 16	Normal analysis
24	Sample 17	Normal analysis
25	Sample 18	Normal analysis
26	Sample 19	Normal analysis
27	Sample 20	Normal analysis
28	Sample 20 - LFM(50ppb)	Recovery of 80-120%
29	Sample 20 - LFMD (50ppb)	RPD ± 15%
30	ECCS (200ppb)	Recovery of 90-110

Table V: Determination of Method Detection Limit And Retention Time Window

Perchlorate Actual Conc. (µg/L)	Retention Time (mins)	Perchlorate Measured Conc. (µg/L)	SD	MDL

2.5	8.96	2.02	0.164	0.5	
2.5	8.67	2.09			
2.5	8.95	2.35			
2.5	8.92	2.13			
2.5	8.69	1.95			
2.5	8.69	1.91			
2.5	8.92	2.28			

Average = 8.82

Table VI: Calculation of MDL

Sample Number		Measured Value	
1	2.02	-0.08	0.006
2	2.09	-0.01	0.000
3	2.35	0.25	0.063
4	2.13	0.03	0.001
5	1.95	-0.15	0.023
6	1.91	-0.19	0.036
7	2.28	0.18	0.032
X	2.10		
S	0.164		
MDL	0.5		

Table VII: Determination of Maximum Conductivity Threshold
(Perchlorate fortified at 25 µg/mL)

Sample	Conductivity	RT	Measured	% Rec	A/H ratio	PDA/H %
LFB	<1	8.87	23.4	94	0.185	0.00
MA (200)	1736	8.78	23.1	92	0.208	12.4
MA (300)	2508	8.78	23.8	95	0.214	15.8
MA (400)	3309	8.74	23.2	93	0.218	18.0
MA (500)	4108	8.75	22.6	90	0.231	25.1
MA (600)	4835	8.73	22.3	89	0.239	29.3
MA (800)	6269	8.71	21.6	86	0.251	35.7
MA (1000)	7805	8.68	20.9	84	0.273	47.6

Extraction and Cleanup of Tissue Samples to be Analyzed for Perchlorate Using Ion Chromatography

OBJECTIVE

To describe the procedures for (1) extracting tissue samples and (2) cleaning up extracts of tissue samples to be analyzed for the perchlorate anion. Samples will be extracted using the accelerated solvent extraction (ASE) and analyzed for perchlorate using ion chromatography (IC).

HEALTH AND SAFETY

Proper lab attire including scrubs, lab coat, gloves, and safety glasses should be worn at all times.

PERSONNEL/TRAINING RESPONSIBILITIES

Any TIEHH employee familiar with the equipment and laboratory techniques and trained in this and referenced SOPs may perform this procedure. Users of this method must demonstrate the ability to generate acceptable results, using the procedures described herein.

REQUIRED AND RECOMMENDED MATERIALS

Materials

- stainless steel extraction cell
- Collection vial (60 mL)
- Cellulose filter
- Glass beakers (50 mL)
- Volume adjustable pipetter
- SPE columns
- Analytical balance
- Filters (Gelman IC Acrodisc, P/N 4485, or equivalent)
- Oven
- Scissors
- Graduated cylinder (50 mL)
- SOP AC-4-04-01
- Disposable pipet tips
- SPE vacuum manifold
- Polypropylene funnel

Reagents

- milli-Q water (18 mΩ)

PROCEDURES

Summary of Method

A measured weight of air-dried tissue sample is extracted using water as the solvent and accelerated solvent extraction (ASE). A portion of the extract (typically ≤ 1 mL) is cleaned using solid phase extraction (SPE) to remove interferences in the extract. The choice of SPE varies with the type of extract as certain phases provide better cleanup than others for certain sample types (e.g. As reported in the literature (Ellington and Evans, 2000), alumina works well with plant extracts). Analysis is completed by injecting a dilution of the cleaned extract into an ion chromatograph equipped with a conductivity detector.

Before operating the ASE, users should be familiar with TIEHH SOP AC-4-04-01.

All glassware and materials should be rinsed with milli-Q (18 mΩ) water. Users of this SOP should refer to TIEHH SOP AC-1-01-01.

Solvent Selection and Preparation for ASE.
1. Fill the solvent reservoir on the ASE with milli-Q (18 mΩ) water.
2. Make sure the in-line filter in the solvent reservoir rests on the bottom of the reservoir to prevent air from being drawn through the line.
3. Hand-tighten the lock ring cap on the solvent reservoir.

Sample Preparation
1. Weigh out 1- 5 grams of sample. Record the wet weight of the sample.
2. Allow sample to air dry (overnight), then record dry weight.
3. Thoroughly mince the air-dried sample with scissors.
4. Prepare extraction cells by inserting a cellulose filter into the cell.
5. Load sample into cell body with funnel. Be careful to keep cell body threads clean.
6. Hand-tighten top cap of cell body.

Extraction
1. Place cell or cells in the ASE cell tray with the "Dionex" symbol on top.
2. Place collection vials in the ASE vial tray.
3. Use the following conditions for extraction:

Preheat = 0 min.	Pressure = 1500 psi
Static = 1 min.	Temperature = 100 C°
Flush = 50%	Water = 100%
Purge = 60 sec.	Cycle =1

4. Load the method or schedule created.
5. Measure and record the volume of extract obtained from each extraction.

Sample Cleanup
1. Select the appropriate SPE cartridge for the sample.
    laboratory fish: silica (conditioned with milli-Q water)
    vegetation: alumina (conditioned with milli-Q water)
    tadpoles: silica (conditioned with milli-Q water)
    mammal (liver, kidney, thyroid): silica (conditioned with milli-Q water)
    blood: precipitation with ethanol, Dionex OnGuard-Ba, Ag, and H
    lab crayfish: C18, powdered alumina
    damselflies: silica (conditioned with milli-Q water)
    field fish: alumina (conditioned with milli-Q water)
    birds: alumina (conditioned with milli-Q water)

2. Condition the SPE cartridge as appropriate.
3. Place a labeled collection vial in the appropriate slot within the vacuum manifold for collection.
4. Replace top of manifold, making sure needle is in the collection vial.
5. Pipette 0.5 - 1 mL of sample extract into the SPE column.
6. Slowly turn on vacuum and allow sample to completely elute into the collection vial.
7. Completely elute 4 - 4.5 mL of milli-Q water through the SPE column.
8. Turn off vacuum, remove top of manifold, and remove collection vial.

9. Filter the eluate using an IC filter (0.45 µm).

QUALITY CONTROL CHECKS/ACCEPTANCE CRITERIA

Sample blanks (sand) and matrix spikes should be incorporated into the extraction procedure. The use of perchlorate-spiked extracts is also recommended to evaluate potential loss of perchlorate during cleanup.

LITERATURE

Anderson, T. A., and T. H. Wu. 2002. Extraction, cleanup, and analysis of the perchlorate anion in tissue samples. Bulletin of Environmental Contamination and Toxicology. 68:684-691.

Ellington JJ, Evans JJ (2000) Determination of perchlorate at parts-per-billion levels in plants by ion chromatography. J Chrom A 898:193-199